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RESIN RESEARCH LABORATORIES, INC.
408 ADAMS STREET
NEWARK 14, N. J.
MARKET 2-5251

INVESTIGATION OF NEW TYPE POLYMERS TO BE USED IN PYROTECHNIC FUELS FOR THERMAL DISSEMINATION OF AGENTS

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INVESTIGATION OF NEW TYPE POLYMERS TO BE USED IN PYROTECHNIC FUELS FOR THERMAL DISSEMINATION OF AGENTS

Dr. Alan E. Weinberg
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1.0 ABSTRACT

During the first two months of investigation into the production of anhydrous syrups from simple sugars, we studied the following reactions:

1. Sugar pyrolysis.
2. Sugar-formaldehyde reactions.
3. Sugar condensations with nitro compounds.
4. Sugar reactions with polyols.

Thus far we have obtained our most promising results with dipropylene and diethylene glycol reaction products with glucose. The pyrolysis experiments have all led to the formation of glassy solids.

2.0 PYROLYSIS OF SUGARS

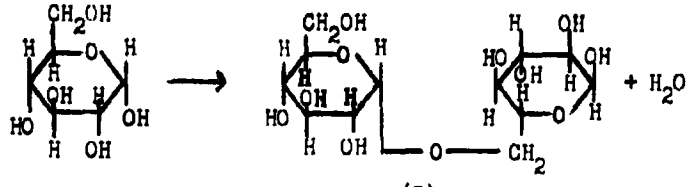
2.1 Introduction

The objective of this phase of the project is to prepare liquid products by pyrolyzing sugars under various conditions. Pyrolysis of sugars results in the formation of anhydrides[1,2,3] which readily tend to polymerize; or in the formation of glycosides.

2.2 Discussion and Results

Anhydrides of sugars are prepared through the dehydration of sugars by use of heat and acidic catalysts. Glycosides are prepared by the condensation of the anomeric hydroxyl, the hydroxyl attached to C-1 in aldohexoses, with a hydroxyl of the same molecule or that of an external molecule.

Pyrolysis of α-D-glucose could give the glycoside (I):



(I)

The thermal dehydration of α-and β-D-glucose yields compounds of higher molecular weight in the di- and tri-saccharide range, according to the work of C. D. Hurd.[4]

Our attempts to prepare liquid products through pyrolysis were unsuccessful. In many cases glassy solids were obtained. In view of the nature of these products, no attempts were made to characterize them.

2.3 Experimental

Pyrolysis was carried out under the conditions listed in Tables 2.1 and 2.2.

TABLE 2.1

PROCEDURES USED FOR PYROLYSIS OF SUGARS

No.	Method	Results
1	Thermal Dehydration without Catalyst	Glassy Solids
2	Thermal Dehydration with Catalyst*	" "
3	Thermal Dehydration under Nitrogen	" "
4	Thermal Dehydration with Catalyst under Nitrogen	" "
5	Thermal Dehydration under Reduced Pressure	" "
6	Thermal Dehydration with Catalyst under Reduced Pressure	" "

* p-toluenesulphonic acid (p-tsa)

TABLE 2.2

DATA ON PYROLYSIS OF SUGARS

Expt. No.	Sugar, Moles			Water, Wt., % Added	P-tsa, Wt., %	Procedure as from Table 2.1	Reaction Conditions			Physical Form of Product		
	Glucose	Lactose	Sucrose				Temp., °C	Pressure	Time, Hr.	Color*	State	Tackiness
2-1	-	-	0.585	-	-	5	95±5	33 mm	1.0	Brown	Glassy Solid	None
5-1	-	-	0.585	-	-	"	100-167	"	2.5	"	"	"
7-1	-	-	0.585	-	-	"	96-172	"	4.0	"	"	"
21-1	0.100	-	-	-	-	1	145-165	Atmospheric	0.8	Orange	Resin-ous	Slight
21-2	0.100	-	-	-	-	"	160±5	"	"	"	"	"
21-3	0.100	-	-	-	-	"	"	"	"	"	"	"
21-4	0.10	-	-	-	-	"	"	"	"	"	"	"
39-1	-	0.100	-	-	-	"	192±1	"	0.5	White	Powder	None
39-2	-	0.100	-	-	-	2	"	"	0.5	"	"	"
39-3	-	0.100	0.100	-	0.5	1	"	"	"	Black	"	"
39-4	-	-	0.100	-	-	2	"	"	"	Black	Solid	"
39-5	0.200	-	-	-	0.5	"	190±2	"	0.2	"	"	Slight
39-6	0.050	-	0.050	-	0.5	"	"	"	"	"	"	-
39-7	0.050	0.050	0.100	-	-	1	"	"	"	> 18	"	Slight
39-8	-	-	0.100	-	-	1	"	"	0.5	"	"	"

* Numbers refer to Hellige Comparator Scale.

TABLE 2.2 (Continued)

Expt. No.	Sugar, Moles			Water, Wt., % Added	P-tsa, Wt., %	Procedure as from Table 2.1	Reaction Conditions			Physical Form of Product		
	Glucose	Lactose	Sucrose				Temp., °C	Pressure	Time, Hr.	Color*	State	Tackiness
39-9	0.050	0.050	–	–	–	1	190±2	Atmospheric	0.5	–	–	Slight
42-1	–	0.100	–	33.3	–	1	153-161	"	"	–	–	–
42-2	–	0.100	–	"	0.5	2	"	"	0.3	Amber	Solid	Slight
42-3	–	–	0.100	"	–	1	"	"	"	0	"	None
42-4	–	–	0.100	"	0.5	2	"	"	"	18	Syrup	Considerable
42-5	0.200	–	–	"	0.5	2	157-161	"	"	9	"	"
42-6	0.050	0.050	0.050	33.3	0.5	2	157-161	Atmospheric	0.3	16	Syrup	–
42-7	"	–	0.100	"	"	"	"	"	"	"	"	–
42-8	–	0.050	"	"	"	"	"	"	"	Lt. Br.	Solid	Slight
42-9	0.050	0.100	–	"	"	"	165-170	"	"	"	"	"
42-10	–	"	0.050	"	"	"	"	"	"	13	"	"
52-1	0.200	–	–	–	"	4	140-177	"	0.35	Black	"	"
52-2	"	–	–	–	–	3	"	"	"	Amber	"	"
52-3	"	–	–	–	0.5	6	"	27 mm	"	Black	"	"
52-4	"	–	–	–	–	5	"	"	"	"	"	"
59-1	"	–	–	–	–	5	59-105	1.2 mm	4.0	White	Crystals	None
60-1	"	–	–	–	0.5	5	103-109	1.2 mm	0.5	"	"	"

* – numbers refer to Hellige Comparator Scale.

These experiments were conducted at different temperatures and for different periods of time. In addition, the choice of apparatus was varied. The use of a high-vacuum rotating evaporator was preferred for pyrolysis under reduced pressure and a rubber-stoppered test tube was found sufficient for those at atmospheric pressure or under nitrogen. Heating was accomplished by using an oil-bath.

3.0 FORMALDEHYDE-SUGAR SYRUPS

These may be divided into two classes:

3.1 Acid-Catalyzed

3.2 Base-Catalyzed

3.1.1 Introduction

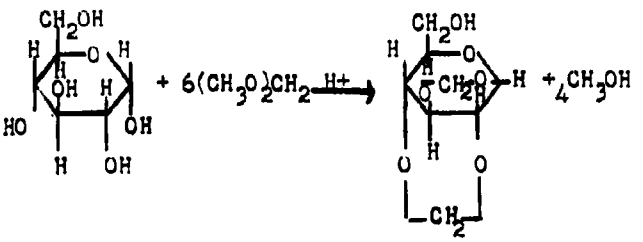
An aldehyde may react with two hydroxyls of a carbohydrate in the presence of acid to give a cyclic acetal. For example, glucose is known to react with formaldehyde to yield the syrupy dimethylene glucose.[5] Thus syrups can be prepared from the reaction of simple sugars with formaldehyde in acidic media.

In the present work, methylal was used in efforts to prepare the methylene derivatives of glucose, lactose, and sucrose.

3.1.2 Discussion and Results

Anhydrous conditions are required since acetals are hydrolyzed by water in the presence of acids. It is believed that methylal, $(CH_3O)_2\ CH_2$, reacts with cis secondary hydroxyls which are β to each other forming methylene bridges through electrophilic substitution. The eliminated protons are accepted by methoxy groups and thus methanol is formed. This mechanism has not been proved in the present work but theoretically it appears convincing.

The reaction of glucose with an excess of methylal in the presence of acid may follow the scheme:



(II)

The excess of methylal is necessary to convert any crystalline monomethylene glucose that may be formed into dimethylene glucose. Acid hydrolysis of the product and the formation of methanol support the above equation. In addition, the fact that at the end of the reaction the product is soluble in the methanol-methylal mixture further convinces us that the desired reaction has gone to completion.

The reaction, using the three sugars separately, yielded heavy syrups. Reaction data, physical properties, and evidence of reaction may be found in Table 3.1.

TABLE 3.1

REACTION OF METHYLAL AND SUGARS - ACID-CATALYZED

Expt. No.	Reactants, Moles				Catalyst, Moles Conc. H_2SO_4				Physical Form of Product		
	Glucose	Lactose	Sucrose	Methylal		Temp., °C	Time, Hr.	Yield, Gm.	Color	State	Gardner Viscosity
4-1	-	-	0.035	3.00	0.056	45	2.00	/	Lt. Br.	Syrup	> Z-8
6-1	-	-	0.350	6.00	0.112	"	4.25	179.5	Dk. Br.	"	"
8-1	0.50	-	-	"	"	43	7.00	169.5	Lt. Br.	"	"
11-1	-	-	0.390	"	0.056	"	"	125.0	Bl.-Blk.	"	"
14-1	1.00	-	-	9.00	"	45	16.00	248.0	Lt. Br.	"	"
17-1	-	0.50	-	6.00	"	"	20.50	91.0	" "	"	"
35-1	-	"	-	"	0.140	44	9.25	233.0	" "	"	"
40-1	-	"	-	"	"	"	2.00	223.0	" "	"	"
53-1	1.0	-	-	"	"	45	7.00	207.0	" "	"	"
56-1	-	-	1.00	"	"	"	5.00	240.0	Dk. Red	"	"

3.1.3 Experimental

The following procedure for the preparation of dimethylene glucose (II) is representative of the methods used for the reactions described in Table 3.1.

3.1.3.1 Preparation of Dimethylene Glucose

In a 1 l. four-necked flask equipped with stirrer, condenser with drying tube, thermometer, dropping funnel, and nitrogen inlet tube were placed 180 g. (1.0 m) anhydrous glucose and 456 g. (6.0 m) anhydrous methylal. To the stirred mixture, under nitrogen, were added drop-wise 25 cc. (0.14 m) conc. sulfuric acid. After the addition of acid, which typically took 10 minutes, the reaction mixture was heated to 45°C and allowed to reflux for 7 hrs.

The mixture was then transferred to a 2 l. Erlenmeyer flask, made slightly alkaline (pH 7.5) by the addition of sodium methoxide in methanol and filtered through a Buchner funnel. The filtrate was transferred to a tared 1 l. round-bottom flask and connected to a high-vacuum rotating evaporator to remove the methanol-methylal mixture. The product (207 g.) obtained was a light-brown, heavy syrup.

3.2.1 Introduction

Reactions of sugars with formaldehyde in the presence of bases are not reported in the literature, but there is reason to believe that aldose and ketose sugars should react with formaldehyde in

aldol-type condensations. It is the purpose of this phase of our work to prepare syrups from such reactions.

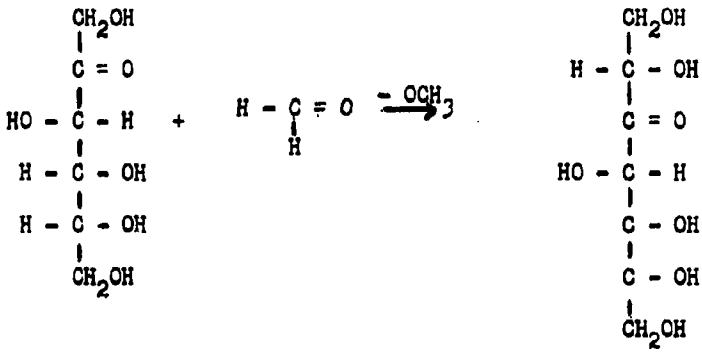
3.2.2 Discussion and Results

Since some sugars contain hydrogens α to the carbonyl group, they should condense with formaldehyde. It seems reasonable to expect a variety of products from such a condensation. Besides the possibility of the formation of diastereoisomers from the creation of new asymetric centers, we can expect the sugars to condense with themselves.

Sucrose cannot undergo an aldol-type condensation since it is not a reducing sugar, but on hydrolysis gives glucose and fructose, which readily do. When this was attempted, heavy syrups were obtained. Because of the possibility of the formation of various mixtures of products from any one of these reactions, we found it impractical to characterize these reaction-products. However, we felt that some proof of reaction was warranted. In this respect, it was observed that the reaction-mixture consisted of a solution shortly after the addition of the sugar to the mixture of paraformaldehyde and sodium methoxide in methanol. Further proof was obtained by making the 2,4 - dinitrophenyl-hydrozone of the syrup and comparing its melting point with that of the same derivative of the starting reducing sugar. The specific reaction which we checked by this method yielded a derivative with a decomposition temperature above 210°C

compared to the glucose derivative which melts at 88°C.

The ketoheptose (III) could be prepared from the reaction with the open-chain representation of fructose according to the following scheme:



(III)

Aldol condensations were run using glucose, and on the hydrolysis products of lactose and sucrose. In general, light-brown syrups of extremely high viscosities were obtained.

3.2.3 Experimental

The following procedure for the preparation of syrupy products from the reaction of glucose-fructose with formaldehyde was used for the reactions listed in Table 3.2.

3.2.3.1 Preparation of Syrups from GLUCOSE-FRUCTOSE and Formaldehyde

In a 2 l. four-necked flask equipped with a stirrer, powder-addition funnel, condenser topped with drying tube,

TABLE 3.2

REACTION OF FORMALDEHYDE AND SUGARS - BASE-CATALYZED

Expt. No.	Reactants, Moles				Catalyst*				Physical Form of Product		
	Sugar										
	Glucose	Fructose	Galactose	Formaldehyde		Temp., °C	Time, Hr.	Yield, Gm.	Color	State	Gardner Viscosity
30-1	0.25	-	-	2.0	0.218	30-35	12.5	/	Lt. Br.	Semi-solid	> Z-8
51-1	"	0.25	-	3.5	0.373	28-40	2.0	/	Beige	Syrup	"
65-1	"	-	0.25	4.0	0.306	29-61	4.4	/	Lt. Br.	"	"
85-1	"	0.25	-	3.3	0.140	30-53	2.75	134	" "	Syrup	"

* Sodium methoxide, moles per liter of methanol.

nitrogen inlet tube and thermometer, containing 650 ml. of freshly prepared 0.14 M sodium methoxide in methanol under nitrogen, were added 100 gms. of paraformaldehyde. The mixture was heated to 30°C and the sugar was added in 10 g. portions over a period of 1 hr. After the addition of sugar, the temperature was gradually increased to 51-53°C and maintained within this range until all had reacted.

At the end of the reaction, the mixture was neutralized with glacial acetic acid, filtered, and the filtrate was then transferred to a 1 l. round-bottom flask connected to a high-vacuum rotating evaporator, and the methanol and excess formaldehyde removed under reduced pressure.

4.0 CONDENSATIONS OF SUGARS WITH NITRO-COMPOUNDS

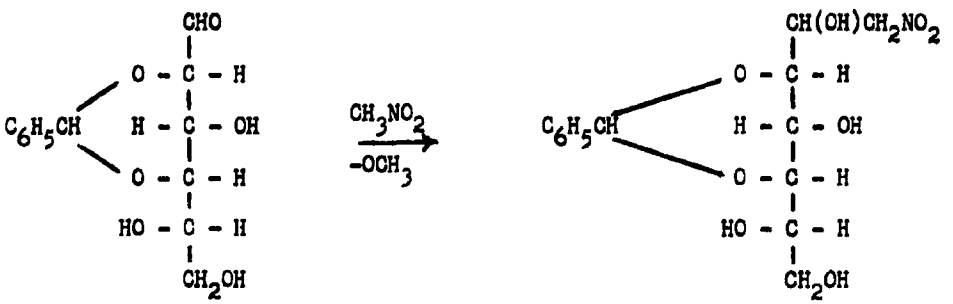
These may be grouped in two classes:

4.1 Condensations with Nitroalkanes

4.2 Condensations with Nitroalcohols

4.1.1 Introduction

Nitroalkanes containing at least one hydrogen α to the NO_2 group readily undergo base-catalyzed condensations with compounds containing carbonyl groups.[6] For example, nitromethane reacts with 2,4-benzylidene-l-xylopyranose in the presence of methanolic sodium methoxide to give the nitro-alcohol (IV).



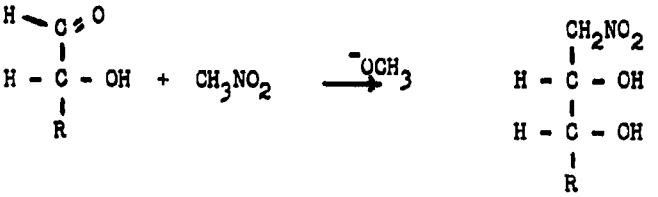
(IV)

It suggests possibilities for lengthening the chain of a reducing sugar and simultaneously introducing a nitro-group, which enhances the reducing power of the sugar. In view of this, efforts were made to prepare syrupy substituted sugars from the base-catalyzed condensation of sugars with nitroalkanes.

4.1.2 Discussion and Results

Since nitroalkanes undergo aldol condensations with carbonyl compounds in the presence of base, they should, therefore, react with reducing sugars under similar conditions. A carbanion, which is believed to be formed from the action of the base on the nitroalkane, is a powerful nucleophile, and should attack the carbonyl carbon to produce the nitroalcohol. Here again, a new pair of diastereoisomers is introduced and the products are expected to be syrupy.

The equation for the reaction presumably is as follows:



(V)

4.1.3 Experimental

Except for minor changes, the procedure used for the reaction of nitroalkanes with sugars in the presence of base was similar to that described in 3.2.3.1.

Reaction data and physical properties of products are given in Table 4.1.

TABLE 4.1

REACTION OF SUGARS WITH NITROMETHANE

Expt. No.	Reactants, Moles			Catalyst*			Physical Form of Product		
	Sugar								
	Glucose	Lactose	Nitromethane		Temp., °C	Time, Hr.	Color	State	Gardner Viscosity
13-1	0.15	-	1.5	0.250	28-60	2.25	Br.	Syrup	> Z-8
16-1		0.08	1.5	"	26-60	11.5	"	"	"

* Sodium methoxide, moles per liter of methanol.

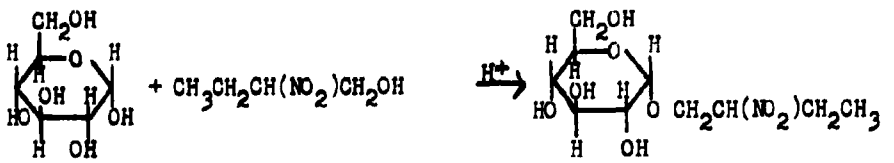
4.2.1 Introduction

The reaction of nitroalcohols with sugars is not reported in the literature; however, these alcohols can react with sugars in the presence of acid to give glycosides.

A mixture of the glycoside and nitroalcohol might be syrupy and the presence of the nitro group in the sugar molecule would enhance its reducing power.

4.2.2 Discussion and Results

The reaction between glucose and 2-nitro-1-butanol may give the glycoside (VI):



(VI)

An excess of nitroalcohol is necessary for the reaction to go to completion. Hence, the nitroalcohol must be a liquid in order that the products be syrupy. When condensations were run, solid products were obtained in cases where the molar ratio of sugar to nitroalcohol was 1:1 and 1:2. A syrup was prepared when the ratio was 1:4. Although no tests have been run as yet, it is felt that proof of reaction can be found in any of three ways. Water is

formed in these reactions and thus a quantitative check is possible. The second involves the isolation and purification of the glycoside so that the presence of the nitro group may be detected, both qualitatively and quantitatively. Thirdly, the reaction mixture may be tested for the presence of a carbonyl group.

4.2.3 Experimental

The above condensations were run in tared 1 l. round-bottom flasks connected to high vacuum rotating evaporators. The flasks were immersed in oil-baths at 100±5°C and rotated for a period of 1hr. under reduced pressure.

Reaction data are listed in Table 4.2.

TABLE 4.2

REACTION OF SUGARS WITH 2 - NITRO - 1 - BUTANOL (NB)

Expt. No.	Reactants, Moles			Catalyst				Physical Form of Product			
	Sugar										
	Glucose	NB	Methanol	P-tsa, Wt. %	Temp., °C	Time, Hr.	Yield, Gm.	Color	State	Gardner Viscosity	Pressure, mm
76-1	0.2	0.2	6.3	0.5	100±5	1.0		Dk. Grn.	Solid	/	27±5
78-1	"	0.4	-	"	"	"	74.7	"	Solid	/	"
79-1	"	0.8	-	"	"	0.5	129	Amber	Syrup	> Z-8	"

* Sodium methoxide, moles per liter of methanol.

5.0 REACTION OF SUGARS WITH POLYHYDROXYL COMPOUNDS

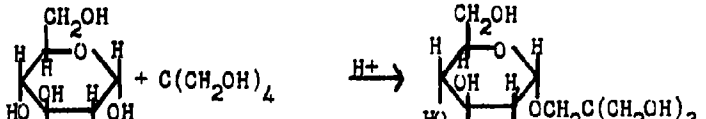
5.1 Introduction

Very little work is published on the condensation of sugars with polyols although such reactions take place readily. The condensation of a reducing sugar with a polyol is a convenient way of adding more hydroxyl groups to the sugar molecule.

It was felt that the reaction products would undoubtedly be syrupy and their viscosities could be varied, depending on the choice and concentration of the polyol. In fact, the desired glycoside could be constructed as a model and then synthesized.

5.2 Discussion and Results

A reducing sugar may react with polyhydroxyl compounds in the presence of acid to form glycosides of the type (VII):



(VII)

The fact that this reaction does not take place in the absence of catalyst was demonstrated in several preliminary experiments in which mixtures of polyol and sugar, with and without catalyst, were run under identical conditions. No conclusive evidence of reaction was obtained in

the uncatalyzed runs.

A second, third, or fourth molecule of sugar can further react with the glycoside. However, when the ratio of sugar to polyol was greater than 1:1, semi-solids were obtained.

Evidence of reaction can be found in the fact that water is eliminated in the reaction. Thus, if this water is collected, a quantitative yield may be calculated. Tests on the purified product for the presence of a carbonyl group further indicate that the reaction takes place. In addition, physical changes in the reaction mixture give further proof of reaction.

An exotherm was found in the condensation of one mole of diethylene glycol, $(HO\ CH_2\ CH_2)_2O$, with glucose.

It was not sufficient, however, to maintain the reaction-mixture at the desired temperature and for the desired time.

5.3 Experimental

Several techniques were used for the preparation of glucosides. The following procedure was found to be optimum.

Required molar quantities of polyol and sugar were mixed with 5% p-toluenesulfonic acid and charged to a tared round-bottom flask which was then connected to a rotating evaporator. The rotating flask was immersed in an oil bath at $100\pm5°C$ for 1 hr. under (27 ± 5mm) reduced pressure. At the end of the reaction, the flask with product and the distillate were weighed.

Reactions carried out at atmospheric pressure were run either in test tubes or reaction flasks with necessary equipment.

Experimental details are summarized in Tables 5.1-5.

TABLE 5.1

REACTION* OF TRIMETHYLOLPROPANE (TMP) WITH GLUCOSE

Expt. No.	Reactants, Moles: Glucose	TMP	P-tsa Wt.%	Temp., °C	Pressure	Time, Min.	Color	State	Viscosity	DNPH[7]	Tollens[7]	Approx. No. of Moles of H_2O Eliminated
22-1	0.1	0.07	–	162-165	Atmospheric	22	/	Semi-solid	/	–	+	0.1
22-2	"	0.14	–	"	"	"	1	"	> Z-8	–	+	"
22-3	"	"	5.0	164-165	"	8	/	Syrup	> Z-8	–	+	"
22-4	"	"	"	157-165	"	4	4-5	"	"	–	–	"
22-5	"	0.28	–	"	"	20	1	"	"	–	+	"
22-6	"	"	5.0	157-158	"	7	4-5	"	"	–	–	"
24-1	"	0.09	"	143-149	"	10	/	Semi-solid	/	–	–	"
24-2	"	"	0.5	"	"	"	18	"	/	–	–	"
24-3	"	0.18	"	149-155	"	6	9	Syrup	> Z-8	–	–	"
24-4	0.2	0.09	"	"	"	21	18	Solid	/	–	–	"
26-1	0.2	0.2	"	150-153	"	10	/	Syrup	> Z-8	–	–	0.2
26-2	0.2	"	–	"	"	"	0	Solid	/	–	+	"
26-3	0.2	0.3	0.5	"	"	"	/	Syrup	> Z-8	–	–	"
26-4	0.4	0.2	"	"	"	"	1	Semi-solid	> Z-8	–	–	0.4
31-1	0.1	0.3	"	115-124	"	5	"	Syrup	"	–	–	0.1
31-2	"	0.4	"	"	"	15	"	"	"	–	–	"
31-3	0.3	0.1	"	115-146	"	40	12	"	> Z-8	+	+	0.3

* Reactions were run in test tubes immersed in an oil bath.

TABLE 5.2

REACTION OF DIPROPYLENE GLYCOL (DPG) WITH GLUCOSE

Expt. No.	Reactants, Moles: Glucose	DPG	P-tsa Wt.%	Temp., °C	Time, Min.	Color	State	Viscosity	DNPH	Tollens	Approx. No. of Moles of H_2O Eliminated[2]
23-1	0.2	0.20	-	157	14	0	Solid	/	+	+	0.2
23-2	"	"	0.5	143-147	"	9-10	Syrup	Z-8	-	-	"
23-3	0.1	"	"	143-148	"	Lt. Br.	Semi-solid	/	-	-	0.1
23-4	"	"	"	"	"	12	Syrup	> Z-8	-	-	"
23-5	"	0.10	"	"	"	11	"	Z-8	-	-	"
32-1	"	"	"	124-134	15	5	"	"	-	+	/
32-2	"	0.20	"	124-134	15	4	"	Z-2	-	+	/
32-3	"	0.30	"	126-136	10	1	"	L	-	+	/
32-4	"	0.40	"	"	"	1	"	G	-	+	/
32-5	0.2	0.10	"	"	"	0	Non-homogeneous	/	+	+	/
34-1	0.1	"	"	145-147	15	17	Syrup	U	-	+	0.1
34-2	"	0.20	"	145-157	"	9	Syrup	Z-1	-	+	"
34-3	"	0.30	"	"	"	11	"	U	-	+	"
34-4	"	0.40	"	146-152	14	13	"	O	-	+	"
34-5	0.2	0.10	"	"	"	14	"	> Z-8	-	+	0.2
68-1[RP]	1.0	1.00	-	100±5	60	0	Non-homogeneous	/	+	+	/
69-1[RP]	1.0	"	0.5	"	"	12	Syrup	> Z-8	-	+	0.8
70-1[RP]	1.0	0.50	"	"	"	Dk. Br.	Solid	/	+	+	0.5
71-1[RP]	0.5	1.00	"	"	"	5	Syrup	Z-7	-	-	"
72-1[RP]	"	0.625	"	"	"	11	"	> Z-8	-	-	"
73-1[RP]	"	0.750	"	"	"	6	"	"	-	-	"

RP - These reactions were run under 27±5mm pressure.

TABLE 5.3

REACTION OF GLYCEROL WITH GLUCOSE

Expt. No.	Reactants, Moles: Glucose	Glycerol	P-tsa, Wt. %	Temp., °C	Time, Min.	Color	State	Viscosity	DNPH	Tollens	Approx. Moles of H_2O Eliminated
33-1	0.10	0.10	0.5	136-143	10	12	Syrup	Z-8	-	-	0.1
33-2	0.20	0.10	0.5	"	"	13	"	"	-	+	"
33-3	0.30	0.10	0.5	"	"	14	Solid	/	+	+	"
33-4	0.10	0.20	0.5	143-149	"	11	Syrup	Z-6	-	+	"
33-5	0.10	0.30	0.5	"	"	11	"	Z-4	-	-	"

TABLE 5.4

REACTION OF PENTAERYTHRITOL (PENTA) WITH SUGARS

Expt. No.	Reactants, Moles					Evidence of Reaction						
	Glucose	Sucrose	Lactose	Penta.	P-tsa, Wt. %	Temp., °C	Time, Min.	DNPH	Tollens	Approx. Moles of H_2O Eliminated[2]	Color	State
44-1	0.10			0.1	–	162-164	20	+	+	/	0	Non-homogeneous
44-2	0.10			"	0.50	"	"	–	–	0.1	13	Semi-solid
44-3	0.2			"	"	"	"	+	+	"	13	Solid
44-4	0.3			"	"	159-162	"	+	+	"	13	"
44-5	0.4			"	"	"	"	+	+	"	18	"
47-1			0.025	0.025	"	147-164	28	–	–	/	18	"
47-2			0.050	"	0.50	"	"	–	–	/	"	"
47-3			0.075	"	0.50	"	"	–	–	/	"	"
47-4			0.100	"	0.50	156-161	30	–	–	/	"	"
47-5			0.025	"	–	"	"	–	–	/	"	"
47-6		0.025		"	0.50	"	"	–	–	/	Blk.	"
47-7		0.050		"	"	154-155	20	–	–	/	18	"
47-8		0.075		"	"	154-155	"	–	–	/	18	"
47-9		0.100		"	"	153	14	–	–	/	18	"
47-10		0.025		"	–	"	30	–	–	/	White	"

TABLE 5.5

REACTION OF DIETHYLENE GLYCOL (DEG) WITH GLUCOSE

Expt. No.	Reactants, Moles		Catalyst Concn., Wt.%	Reaction Conditions			Physical Form of Product			Evidence of Reaction		
	Glucose	DEG	P-tsa	Temp.,°C	Time, Min.	Pressure	Color	State	Viscosity	DNPH	Tollens	Moles H_2O Elimin.
37-1	0.10	0.10	0.5	165	15	Atmospheric	17	Syrup	Z-8	-	+	/
37-2	0.20	0.10	0.5	165	15	"	18	"	> Z-8	-	+	/
37-3	0.10	0.20	0.5	165	15	"	18	"	V	-	+	/
45-1	1.0	2.0	0.5	30-164	200	"	Black	"	Z-1			1.0
48-1*	1.0	2.0	0.5	30-100	60	"	4	"	Z-1	-	-	0.3
57-1*	1.0	1.0	0.5	30-133	70	"	11	"	> Z-8	-	-	0.5
61-1	2.0	2.0	0.5	32-105	67	27 mm	2	"	> Z-8	-	-	2.0
62-1	1.0	1.25	0.5	$100^{+}_{-}5$	60	27 mm	4	"	> Z-8	-	-	1.0
63-1	1.0	1.5	0.5	$105^{+}_{-}5$	60	27 mm	6	"	Z-8	-	-	1.0
64-1	1.0	1.75	0.5	$105^{+}_{-}5$	60	27 mm	3	"	Z-6	-	-	1.0
66-1	2.0	1.0	0.5	$105^{+}_{-}5$	60	27 mm	4	"	> Z-8	+	+	1.5
67-1	1.0	1.0	-	$105^{+}_{-}5$	60	27 mm	White	Solid & Liquid	/	+	+	0.33

* Reaction was run under nitrogen.

6.0 FEASIBILITY EXPERIMENTS

In order to determine whether the syrups prepared by the reaction of dipropylene and diethylene glycol with glucose would burn, several small charges were made up in anti-dim cans with red-dye simulant and potassium chlorate. These experiments are summarized in Table 6.1.

Our results indicate that the syrups will burn sufficiently well for use in pyrotechnic devices for dispersion of agents. We have prepared samples of syrup for further studies to be carried out by Army Chemical Center.

TABLE 6.1

FEASIBILITY STUDIES FOR PYROTECHNIC MIXTURES

Expt. No.	Syrup Description	Weight (Gms.) Syrup	Dye	$KClO_3$	Time (Sec.) Burning Before Smoke	Red Smoke	Description of Residue	Remarks
74-1	48-1 - 1 mole glucose 2 moles DEG	5	10	5	10"	60"	Powdery, brittle ash. 7 gms.	Bright red smoke. Large amount of starter mix used.
77-1	71-1 - 1 mole glucose 2 moles DPG	5	10	5	9"	51"	Powdery, brittle ash with some unburned dye remaining. 11 gms.	Bright red smoke, slightly intermittent due to poor packing. Approx. 3 gms. starter mix.
77-2	64-1 - 1 mole glucose 1.75 moles DEG	5	10	5	9"	68"	Powdery, brittle ash. 6.5 gms.	Bright red smoke. Approx. 3 gms.starter mix used.
86-1	61-1 - 1 mole glucose 1 mole DEG	6	10	5	2"	160"	Powdery, brittle ash. 9.5 gms.	Bright red smoke. 1. 5 gms. starter mix used.

7.0 CONCLUSIONS AND FUTURE WORK

At this point in our investigation of anhydrous sugar syrups for pyrotechnic use our most promising results have been with the polyol-sugar glycoside reactions. Formaldehyde-sugar reaction products have been too viscous for test thus far and the nitro-alcohol reactions have not yet been investigated to a great extent. Changes in technique and reactant combinations may possibly yield useful syrupy products in the future.

In the next bimonthly period we will continue to investigate the foregoing reactions to produce syrups of acceptable viscosity and burning characteristics for pyrotechnic uses. It is expected that a close liaison will be established with Army Chemical Center to test promising syrups at Edgewood as they are produced.

We plan to begin investigation of reactions of the syrups to yield crosslinked pyrotechnic mixtures that will show no tendency to flow in storage or due to recoil forces that may be encountered in some munitions. Likely candidates for crosslinking hydroxyl groups include:

1. Aluminum chelates
2. Organo titanium compounds
3. Diacid chlorides
4. Dialdehydes
5. Diisocyanates

8.0 BIBLIOGRAPHY

1. Amé Pictet et al., Comp. rend. 171, 243 (1920).

2. Amé Pictet et al., Helv. Chim. Acta, 3, 645 (1920); ibid., 4, 613 (1921); ibid., 5, 444 (1922); ibid., 6, 129 (1923); ibid., 7, 295 (1924).

3. N. K. Richtmeyer and C. S. Hudson, J. Am. Chem. Soc., 61, 214 (1939); ibid., 62, 961 (1940).

4. C. D. Hurd, J. Or. Chem., 14, 680-91 (1949).

5. C. A. Lobry de Bruyn and W. Alberda Van Ekenstein, Rec. Trav. Chim., 22, 159 (1903).

6. J. C. Snowden and H. O. L. Fischer, J. Am. Chem. Soc., 66, 1312 (1944); ibid., 67, 1713 (1945); ibid., 69, 1048 (1947); ibid., 71, 1897 (1949); ibid., 72, 3325 (1950); ibid., ibid., 73, 4662, 5496 (1951).

7. D. Davidson and D. Perlman, A Guide to Qual. Or. Anal., (3rd ed., Brooklyn, N. Y.: Davidson and Perlman, 1961) pages 49, 52.